

6. ANALYTICAL METHODS

The purpose of this chapter is to describe the analytical methods that are available for detecting and/or measuring and monitoring tin in environmental media and in biological samples. The intent is not to provide an exhaustive list of analytical methods that could be used to detect and quantify tin. Rather, the intention is to identify well-established methods that are used as the standard methods of analysis. Many of the analytical methods used to detect tin in environmental samples are the methods approved by federal agencies such as EPA and the National Institute for Occupational Safety and Health (NIOSH). Other methods presented in this chapter are those that are approved by groups such as the Association of Official Analytical Chemists (AOAC) and the American Public Health Association (APHA). Additionally, analytical methods are included that refine previously used methods to obtain lower detection limits, and/or to improve accuracy and precision.

Tin is usually determined as the total metal, but it may also be measured as specific organotin compounds. Flame atomic absorption analysis is the most widely used and straightforward method for determining tin; furnace atomic absorption analysis is used for very low analyte levels and inductively coupled plasma atomic emission analysis is used for multianalyte analyses that include tin.

6.1 BIOLOGICAL MATERIALS

Methods for the determination of tin in biological materials are summarized in Table 6-1.

Normally, for determination in biological samples, the sample is digested in an oxidizing acid mixture followed by atomic spectrometric determination. Organotin can be extracted from biological samples and determined by atomic spectrometric methods or gas chromatography, usually after derivatization.

6.2 ENVIRONMENTAL SAMPLES

Methods for determination of tin in environmental samples are summarized in Table 6-2.

Tin is readily measured in multielement analyses of air, water, and solid waste samples by inductively coupled plasma atomic emission spectroscopy. For individual analyses of tin, direct aspiration atomic absorption spectroscopy is usually used. Organotin can be extracted from environmental samples and determined by atomic spectrometric methods or gas chromatography, usually after derivatization.

TABLE 6-1. Analytical Methods for Determining Inorganic Tin and Organotin Compounds in Biological Materials

| Sample matrix | Preparation method | Analytical method | Sample detection limit | Percent recovery | Reference |
|-----------------------------------|--|------------------------------------|------------------------|------------------|---------------------------|
| <u>Total inorganic tin</u> | | | | | |
| Biological material ^a | Digestion of biological materials | Atomic spectrometric | No data | No data | Angerer and Schaller 1988 |
| Urine | Digest in oxidizing acid, extract ketone as the cupferon chelate | Colorimetry | <50 µg/L ^b | 98%-106% | Baselt 1988 |
| Urine | Extraction with poly-dithiocarbamate resin, which is ashed | ICP/AES | 2 µg/L | 100±10% recovery | Kneip and Crable 1988 |
| Urine | Extract with resin, ash resin | ICP/AES | 0.1 µg | 100±10% | NIOSH 1984a |
| Food | Digest in oxidizing acid | AAS | No data | No data | AOAC 1984b |
| <u>Organotins and metabolites</u> | | | | | |
| Fruit | No data | Spectrophotometry (dithiol method) | 0.2 µg | -98% | Corbin 1970 |
| Biological materials, tissue | Homogenized, hydrochloric acid added, extracted with ethyl acetate | HPLC/fluorescence ^c | 0.1-1 ng | 91%-100% | Yu and Arakawa 1983 |
| Biological materials | Elution stepwise on silica gel column | AAS | 1.5 ng | 72.7±9.3% | Iwai et al. 1981 |

^aA digestion procedure for metals in biological materials applicable to most metals, including tin.

^bEstimated from sensitivity and linearity data.

^cFluorescence detection after derivitization with Morin reagent

AAS = atomic absorption spectroscopy; HPLC = high performance liquid chromatography; ICP/AES = inductively coupled plasma atomic emission spectroscopy

TABLE 6-2. Analytical Methods for Determining Inorganic Tin and Organotin Compounds in Environmental Samples

| Sample matrix | Preparation method | Analytical method | Sample detection limit | Percent recovery | Reference |
|------------------------------|--|-------------------------|------------------------|------------------|-------------------------------------|
| <u>Total inorganic tin</u> | | | | | |
| Environmental | Digested in oxidizing acid | ICP/MS | 0.04-50 ng/g | 103±3% | Brzezinska-Paudyn and Van Loon 1988 |
| Water | Generate hydride with sodium borohydride or electrolytically, sweep into silica cell heated to 700°C | AAS | 0.02 µg/L | No data | Rains 1982 |
| Water (aqueous solution) | Generate hydride with sodium borohydride or electrolytically, sweep into silica cell heated to 700°C | AAS | 0.5 µg/L | No data | Thompson and Thomerson 1974 |
| Water | Acidify with nitric acid | AAS (direct aspiration) | 0.8 mg/L | No data | APHA 1989c |
| Water | Acidify with nitric acid | AAS (furnace technique) | 5 µg/L | No data | APHA 1989a |
| Water ^a | Acidify with nitric acid | ICP/AES | No data | No data | APHA 1989d |
| Water | Acidify with nitric acid | AAS (direct aspiration) | 0.8 mg/L | No data | EPA 1983a |
| Water | Acidify with nitric acid | AAS (furnace technique) | 5 µg/L | No data | EPA 1983b |
| Sediments, sludges, soils | Acid digestion procedure for subsequent atomic spectrometric analysis | AAS, ICP/AES | Not applicable | Not applicable | EPA 1986a |
| Waste effluent, solid wastes | Acidify with nitric acid, digest if necessary | AAS (direct aspiration) | 0.8 mg/L in water | 96±6% at 4 mg/L | EPA 1986b |
| Pesticide formulations | Form volatile organotin derivatives | GC/FID | No data | No data | Basters et al. 1978 |
| <u>Organotins</u> | | | | | |
| Pesticide | Derivatize, extract with toluene | GC/FID | No data | No data | AOAC 1984a |

TABLE 6-2 (Continued)

| Sample matrix | Preparation method | Analytical method | Sample detection limit | Percent recovery | Reference |
|----------------------------|---|-------------------------|------------------------|--------------------------------|-----------------------------|
| <u>Organotin</u> s (Cont.) | | | | | |
| Air | Adsorbed onto Chromosorb 102 desorption with ethereal hydrochloric acid, methylated | GC/FID | 0.05 µg/m ³ | 93.3±9.3% | Zimmerli and Zimmerman 1980 |
| Air | Adsorption on filter and XAD-2 resin, desorption | AAS (furnace technique) | 1 µg | No data | NIOSH 1984b |
| Water | Acidified, extracted with tropoloin benzene, derivatized | GC/FPD | 100 pg | 96±4% to 103±8% | Maguire and Huneault 1981 |
| Water | Generate hydrides with sodium borohydride, separate hydrides by boiling point | AAS | 2 ng | No data | Hodge et al. 1979 |
| Water | Generate hydride derivatives | AAS | <0.1 µg/L tributyltin | No data | Lee et al. 1989 |
| Water | Extract in n-hexane, produce fluorescent morin derivative | Fluorescence | 0.001-0.5 nmol/mL | 91.3±0.6 to 99.7±0.5% recovery | Arakawa et al. 1983 |

*Tin not listed specifically as an analyte, but can be determined by ICP/AES

AAS = atomic absorption spectrometry; GC/FID = gas chromatography/flame ignition detector; GC/FPD = gas chromatography/flame photometric detector; ICP/AES = inductively coupled plasma atomic emission spectroscopy; ICP/MS = inductively coupled plasma with mass spectrometric detection

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6.3 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of tin is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of tin.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met, would reduce or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.3.1 Data Needs

Methods for Determining Biomarkers of Exposure and Effect. Sensitive and selective methods are available for the detection and quantitative measurement of tin after the sample matrix in which it is contained has been properly treated. Atomic spectrometric techniques provide methods for the determination of tin that have low detection limits, are highly specific, and are readily available (Angerer and Schaller 1988; AOAC 1984b; Kneip and Crable 1988; NIOSH 1984a). Methods for the determination of specific compounds that contain tin are more difficult and less well developed than are methods for the determination of total tin, but this is an important concern because of the widespread use of organotin compounds as preservatives in industry and in other applications.

No methods have been identified that can be used to associate the level and extent of exposure to tin and specific tin compounds with levels of tin in biological materials such as human tissues or fluids. It would be useful to have such methods to make these correlations.

Similarly, no methods have been identified that can be used to directly associate levels of tin and specific tin compounds in biological samples with the onset of adverse health effects. If such methods were available, it would be possible to correlate the level or severity of effects with the level and extent of exposure.

Methods for Determining Parent Compounds and Degradation Products in Environmental Media. Methods for determining tin in water, air, and waste samples with excellent selectivity and sensitivity are well developed and undergoing constant improvement.

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Sampling methodologies for very low level elemental pollutants such as tin continue to pose problems, including nonrepresentative samples, insufficient sample volumes, contamination, and labor-intensive, tedious extraction, and purification procedures (Green and LePape 1987).

6.3.2 On-going Studies

Examination of the literature suggests that studies are underway to improve means for determining tin and other heavy metals in biological samples and environmental media. Improvements continue to be made in detection limits and ease and speed of analysis.